

DETERGENT TABLET

The present invention relates to detergent tablets, especially those adapted for use in washing machines.

Detergent tablets are widely used in particular for auto-dish-washing, and increasingly for washing laundry. These tablets are a possible alternative to detergent powders or detergent liquids. Various types of detergent tablets have been described, for example in . Tablets have the advantage of allowing ease of dosing when compared to liquids or powders. Liquids and powders themselves have the advantage of allowing pre-treatment of fabrics with use of pre-treatment implements such as described for example in EP-A-0 679 751 for liquids or in PCT/US97/13730 for powders. In particular, in the case of PCT/US97/13730, pre-treatment is following a pre-dissolution step for the powder. Such a pre-treatment allows an improvement of the cleaning performance of liquids and powders.

The invention seeks to provide a detergent tablet and a process of using a detergent tablet which allows to maintain the ease of dosing advantage over liquid or powdered detergents, while allowing to obtain the improvement in cleaning performance which exists when pre-treating with liquid or powdered detergents.

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Summary of the Invention

In a first aspect, the object is achieved by providing a detergent tablet, characterised in that at least part of the outer surface of the detergent tablet is semi-solid.

In another aspect, the object of the invention is achieved by a process for washing a substrate comprising the first step of providing a substrate and a detergent tablet, a third step of inserting the substrate and the tablet in a washing machine, the wash taking place normally thereafter, characterised in that it comprises a second step of rubbing the detergent tablet onto the substrate.

Detailed Description of the Invention

The invention relates to a detergent tablet.

By detergent, it should be understood that it has a detergency function, in so far as it contains compounds modifying the surface tension of water when put into an aqueous solution. Typically, this is obtained by use of surfactants. Such a detergency function typically allows the washing of various substrates such as fabrics for laundry wash, or table-ware or kitchen ware for dish-washing.

By tablet, it should be understood a solid block, typically made by compression of a particulate material. This includes pellets or briquettes for example. Typically, a tablet will comprise a main axis, according to which the tablet has a volume substantially defined by the displacement of a given cross-section normal to the main axis along this main axis on a distance which corresponds to the height of the tablet. Typically, the cross-section will be a circle, rectangle or square, although other shape may be considered such as flower, star, or other possible aesthetically attractive shapes. Other tablet forms may include spheres, ellipsoids or similar shapes for example.

As the detergent tablet according to the invention is a solid block, it has an outer surface. According to the invention, at least part of the outer surface is semi-

solid. By semi-solid, it should be understood a state whereby the outer surface is made of a material which is not strictly speaking a solid or a liquid, but which has the consistency for example of a gel. Indeed, it was found that such a state or consistency was fulfilling the object of the invention.

A possible test to use to define an outer surface as semi-solid is defined here. The outer surface to test is first laid onto a piece of substrate, normally a piece of test fabric EMPA Art 300 supplied by EMPA Testmaterialen. The substrate itself is laid flat and fixed onto a hard surface, such as a bench or a table for example, during the test.

Once the outer surface is laid onto the piece of substrate, the portion of the outer surface which is in contact with the piece of substrate is submitted to a pressure normal to the piece of substrate, the pressure being of 3890Pa. The portion of the outer surface which is in contact with the piece of substrate is also submitted to a pressure tangential to the piece of substrate, the pressure being again of 3890Pa. The tangential application of the pressure should be sufficient to produce a displacement of the tablet in a direction parallel to the plane of the substrate, the tablet being displaced onto the substrate, both the tangential and normal pressure being applied simultaneously.

The tangential pressure should be understood as the ratio between, on one hand the component of a force applied to the tablet in a direction which is in the plane of the substrate and, on the other hand, the surface area of contact between the substrate and the part of the outer surface of the detergent tablet which is semi-solid. Similarly, the normal pressure should be understood as the ratio between, on one hand the component of a force applied to the tablet in a direction which is normal to the plane of the substrate and, on the other hand, the surface area of contact between the substrate and the part of the outer surface of the detergent tablet which is semi-solid.

During displacement, the semi-solid surface should leave part of its constituents adhering onto the substrate. During displacement, the portion of the outer surface which is in contact with the piece of substrate is treating a zone of the substrate, the zone having a treatment zone area.

Typically, the portion of the outer surface which is in contact with the piece of substrate is defined as semi-solid when the part of the constituents adhering to the substrate is of at least 5 g per square meter of the treatment zone area. In a preferred embodiment, the constituent adhering to the substrate in the test conditions are of at least 10g per square meter of the treatment zone area, more preferably 15g per square meter, even more preferably at least 20g per square meter and most preferably at least 28g/m².

By "constituent adhering to the substrate" should be understood the constituents remaining on the substrate once the tablet is removed and the substrate turned around so that any part of the tablet which would have been separated from the tablet but would not have adhered to the substrate is not taken into consideration. Indeed, when the substrate is turned around, non adhering parts fall by gravity, so that only adhering constituents remain. The weight of such adhering constituents may simply be measured by the difference of weight of the substrate prior to the test and after having been turned around after the test.

This test is more particularly suited to estimating the "semi-solid" characteristics for laundry applications as the chosen substrate is a piece of fabric. However, the same test should be applied to estimate the "semi-solid" characteristics for other types of applications such as dish-washing, more particularly by use of a substrate such as glass for example, and aiming at obtaining the same results, i.e. the pre-treatment by use of a tablet having a semi-solid part of its outer surface.

It is important that the whole tablet structure should not collapse during such a test, as this would create a messy situation whereby all of the tablet remains would be spread over the substrate. Collapse is typically avoided by using a tablet having a tensile strength of at least 15 kPa, preferably more than 20Kpa.

The semi-solid part of the outer surface may be obtained by use of various materials, such as nonionic surfactants, poly(ethylene glycol), poly(propylene glycol), ethoxylated amine polymers, poly (vinyl alcohol) or gelatin for example.

Various processes may also be used to produce this semi-solid part of the outer surface, sometimes depending on the material used. This could involve melting the raw materials used in the semi-solid composition, mixing thoroughly to obtain a homogeneous dispersion and then pouring the mixture into a mould to set. Particulate material, such as an effervescent system or enzyme prills, can be added during the mixing stage. The mould into which the mixture is poured may contain the tablet, so as to produce a tablet containing a semi-solid layer in one process step. Alternatively the semi-solid layer may be prepared separately and fixed onto the tablet layer in a second step. The semi-solid layer may be fixed onto the tablet using an adhesive or by using heat to slightly melt the semi-solid layer so as to provide good adherence to the tablet on cooling.

In a preferred embodiment, the semi-solid part of the outer surface is a convex part of the whole outer surface. It should be understood by convex part of the whole outer surface that the semi-solid part of the outer surface is bulging towards the outside of the tablet. It should be noted that a flat surface, which would not strictly bulge but would not be recessed either is comprised in "convex" in the this understanding. In this manner, rubbing of the semi-solid part on a substrate is facilitated.

Indeed, in the opposite case where such a surface would not be convex, i.e. would be located in a recess of the tablet, the pre-treatment would require rubbing the substrate to pre-treat onto the semi-solid part of the outer surface located in the recess. This would allow to avoid mess due to deposition of the material composing the semi-solid part of the outer surface: indeed, such a material would then be in a recess. However, this is not a most preferred embodiment.

In order to further facilitate use of the tablet and to avoid mess due to a contact between the semi-solid surface and fingers during use, for example, it is preferred to have an embodiment whereby the outer surface has a second part which is located substantially opposite to the semi-solid part, whereby the second part is solid. Indeed, if for example such a tablet is used for pre-treatment with the hand of a user, the palm or the fingers of the user can be located on the second solid part during pre-treatment in order to avoid soiling of the fingers or of the hand.

In another aspect, the invention also relates to a process for washing a substrate comprising the first step of providing a substrate and a detergent tablet, a third step of inserting the substrate and the tablet in a washing machine, the wash taking place normally thereafter, characterised in that it comprises a second step of rubbing the detergent tablet onto the substrate.

Preferably, the tablet is according to the first aspect of the invention, i.e. it preferably comprises a semi-solid part of the outer surface. Even more preferably, the part of the detergent tablet rubbed during the second step is a portion or the whole of the part of the outer surface of the detergent tablet which is semi-solid.

Most preferably, the process of the invention applies when the substrate is dry prior to the second step. Indeed, this allows better friction during pre-treatment.

Most preferably, the substrate is a piece of fabric, and the washing machine is a laundry washing machine. Indeed, the process preferably applies to the washing of laundry.

In another preferred embodiment, the substrate is a piece of cooking-ware or table-ware, and the washing machine is a dish washing machine. Indeed, the process of the invention is beneficially applied to auto-dish-washing.

The tablets may comprise components such as fragrance, surfactants, enzymes, detergent etc.... Typical tablet compositions for the preferred embodiment of the present invention are disclosed in the pending European applications of the Applicant n° 96203471.6, 96203462.5, 96203473.2 and 96203464.1 for example. Elements typically entering in the composition of detergent tablets or of other forms of detergents such as liquids or granules are detailed in the following paragraphs.

Highly soluble Compounds

The tablet may comprise a highly soluble compound. Such a compound could be formed from a mixture or from a single compound. A highly soluble compound is defined as follow:

A solution is prepared as follows comprising de-ionised water as well as 20 grams per litre of a specific compound:

- 1- 20 g of the specific compound is placed in a Sotax Beaker. This beaker is placed in a constant temperature bath set at 10°C. A stirrer with a marine propeller is placed in the beaker so that the bottom of the stirrer is at 5 mm above the bottom of the Sotax beaker. The mixer is set at a rotation speed of 200 turns per minute.
- 2- 980 g of the de-ionised water is introduced into the Sotax beaker.
- 3- 10 s after the water introduction, the conductivity of the solution is measured, using a conductivity meter.
- 4- Step 3 is repeated after 20, 30, 40, 50, 1min, 2 min, 5 min and 10 min after step 2.
- 5- The measurement taken at 10 min is used as the plateau value or maximum value.

The specific compound is highly soluble according to the invention when the conductivity of the solution reaches 80% of its maximum value in less than 10 seconds, starting from the complete addition of the de-ionised water to the compound. Indeed, when monitoring the conductivity in such a manner, the conductivity reaches a plateau after a certain period of time, this plateau being

considered as the maximum value. Such a compound is preferably in the form of a flowable material constituted of solid particles at temperatures comprised between 10 and 80°Celsius for ease of handling, but other forms may be used such as a paste or a liquid.

Example of highly soluble compounds include Sodium di isoalkylbenzene sulphonate (DIBS) or Sodium toluene sulphonate.

Cohesive Effect

The tablet may comprise a compound having a Cohesive Effect on the particulate material of a detergent matrix forming the tablet. The Cohesive Effect on the particulate material of a detergent matrix forming the tablet or a layer of the tablet is characterised by the force required to break a tablet or layer based on the examined detergent matrix pressed under controlled compression conditions. For a given compression force, a high tablet or layer strength indicates that the granules stuck highly together when they were compressed, so that a strong cohesive effect is taking place. Means to assess tablet or layer strength (also refer to diametrical fracture stress) are given in Pharmaceutical dosage forms : tablets volume 1 Ed. H.A. Lieberman et al, published in 1989.

The cohesive effect is measured by comparing the tablet or layer strength of the original base powder without compound having a cohesive effect with the tablet or layer strength of a powder mix which comprises 97 parts of the original base powder and 3 parts of the compound having a cohesive effect. The compound having a cohesive effect is preferably added to the matrix in a form in which it is substantially free of water (water content below 10% (pref. below 5%)). The temperature of the addition is between 10 and 80°C, more pref. between 10 and 40°C.

A compound is defined as having a cohesive effect on the particulate material according to the invention when at a given compacting force of 3000N, tablets with a weight of 50g of detergent particulate material and a diameter of 55mm have their tablet tensile strength increased by over 30% (preferably 60 and more

preferably 100%) by means of the presence of 3% of the compound having a cohesive effect in the base particulate material.

An example of a compound having a cohesive effect is Sodium di isoalkylbenzene sulphonate.

When integrating a highly soluble compound having also a cohesive effect on the particulate material used for a tablet or layer formed by compressing a particulate material comprising a surfactant, the dissolution of the tablet or layer in an aqueous solution is significantly increased. In a preferred embodiment, at least 1% per weight of a tablet or layer is formed from the highly soluble compound, more preferably at least 2%, even more preferably at least 3% and most preferably at least 5% per weight of the tablet or layer being formed from the highly soluble compound having a cohesive effect on the particulate material.

It should be noted that a composition comprising a highly soluble compound as well as a surfactant is disclosed in EP-A-0 524 075, this composition being a liquid composition.

A highly soluble compound having a cohesive effect on the particulate material allows to obtain a tablet having a higher tensile strength at constant compacting force or an equal tensile strength at lower compacting force when compared to traditional tablets. Typically, a whole tablet will have a tensile strength of more than 5kPa, preferably of more than 10kPa, more preferably, in particular for use in laundry applications, of more than 15kPa, even more preferably of more than 30 kPa and most preferably of more than 50 kPa, in particular for use in dish washing or auto dish washing applications; and a tensile strength of less than 300 kPa, preferably of less than 200 kPa, more preferably of less than 100 kPa, even more preferably of less than 80 kPa and most preferably of less than 60 kPa. Indeed, in case of laundry application, the tablets should be less compressed than in case of auto dish washing applications for example, whereby the dissolution is more readily achieved, so that in a laundry application, the tensile strength is preferably of less than 30 kPa.

This allows to produce tablets or layers which have a solidity and mechanical resistance comparable to the solidity or mechanical resistance of traditional tablets while having a less compact tablet or layer thus dissolving more readily.

Furthermore, as the compound is highly soluble, the dissolution of the tablet or layer is further facilitated, resulting in a synergy leading to facilitated dissolution for a tablet according to the invention.

Tablet Manufacture

The tablet may comprise several layers. For the purpose of manufacture of a single layer, the layer may be considered as a tablet itself.

Detergent tablets can be prepared simply by mixing the solid ingredients together and compressing the mixture in a conventional tablet press as used, for example, in the pharmaceutical industry. Preferably the principal ingredients, in particular gelling surfactants, are used in particulate form. Any liquid ingredients, for example surfactant or suds suppressor, can be incorporated in a conventional manner into the solid particulate ingredients.

In particular for laundry tablets, the ingredients such as builder and surfactant can be spray-dried in a conventional manner and then compacted at a suitable pressure. Preferably, the tablets according to the invention are compressed using a force of less than 100000N, more preferably of less than 50000N, even more preferably of less than 5000N and most preferably of less than 3000 N. Indeed, the most preferred embodiment is a tablet suitable for laundry compressed using a force of less than 2500N, but tablets for auto dish washing may also be considered for example, whereby such auto dish washing tablets are usually more compressed than laundry tablets.

The particulate material used for making a tablet can be made by any particulation or granulation process. An example of such a process is spray drying (in a co-current or counter current spray drying tower) which typically gives low bulk densities 600g/l or lower. Particulate materials of higher density can be prepared by granulation and densification in a high shear batch mixer/granulator or by a continuous granulation and densification process (e.g. using Lodige® CB and/or Lodige® KM mixers). Other suitable processes include fluid bed processes, compaction processes (e.g. roll compaction), extrusion, as well as

any particulate material made by any chemical process like flocculation, crystallisation sentering, etc. Individual particles can also be any other particle, granule, sphere or grain.

The components of the particulate material may be mixed together by any conventional means. Batch is suitable in, for example, a concrete mixer, Nauta mixer, ribbon mixer or any other. Alternatively the mixing process may be carried out continuously by metering each component by weight on to a moving belt, and blending them in one or more drum(s) or mixer(s). Non-gelling binder can be sprayed on to the mix of some, or all of, the components of the particulate material. Other liquid ingredients may also be sprayed on to the mix of components either separately or premixed. For example perfume and slurries of optical brighteners may be sprayed. A finely divided flow aid (dusting agent such as zeolites, carbonates, silicas) can be added to the particulate material after spraying the binder, preferably towards the end of the process, to make the mix less sticky.

The tablets may be manufactured by using any compacting process, such as tableting, briquetting, or extrusion, preferably tableting. Suitable equipment includes a standard single stroke or a rotary press (such as Courtoy®, Korch®, Manesty®, or Bonals®). The tablets prepared according to this invention preferably have a diameter of between 20mm and 60mm, preferably of at least 35 and up to 55 mm, and a weight between 25 and 100 g. The ratio of height to diameter (or width) of the tablets is preferably greater than 1:3, more preferably greater than 1:2. The compaction pressure used for preparing these tablets need not exceed 100000 kN/m², preferably not exceed 30000 kN/m², more preferably not exceed 5000 kN/m², even more preferably not exceed 3000kN/m² and most preferably not exceed 1000kN/m². In a preferred embodiment according to the invention, the tablet has a density of at least 0.9 g/cc, more preferably of at least 1.0 g/cc, and preferably of less than 2.0 g/cc, more preferably of less than 1.5 g/cc, even more preferably of less than 1.25 g/cc and most preferably of less than 1.1 g/cc.

Multi layered tablets are typically formed in rotating presses by placing the matrices of each layer, one after the other in matrix force feeding flasks. As the

process continues, the matrix layers are then pressed together in the pre-compression and compression stages stations to form the multilayer layer tablet. With some rotating presses it is also possible to compress the first feed layer before compressing the whole tablet.

Hydrotrope compound

A highly soluble compound having a cohesive effect may be integrated to a detergent tablet, whereby this compound is also a hydrotrope compound. Such hydrotrope compound may be generally used to favour surfactant dissolution by avoiding gelling. A specific compound is defined as being hydrotrope as follows (see S.E. Friberg and M. Chiu, J. Dispersion Science and Technology, 9(5&6), pages 443 to 457, (1988-1989)):

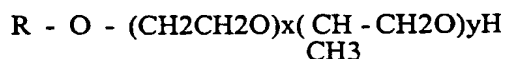
1. A solution is prepared comprising 25% by weight of the specific compound and 75% by weight of water.
2. Octanoic Acid is thereafter added to the solution in a proportion of 1.6 times the weight of the specific compound in solution, the solution being at a temperature of 20°Celsius. The solution is mixed in a Sotax beaker with a stirrer with a marine propeller, the propeller being situated at about 5mm above the bottom of the beaker, the mixer being set at a rotation speed of 200 rounds per minute.
3. The specific compound is hydrotrope if the the Octanoic Acid is completely solubilised, i.e . if the solution comprises only one phase, the phase being a liquid phase.

It should be noted that in a preferred embodiment of the invention, the hydrotrope compound is a flowable material made of solid particles at operating conditions between 15 and 60° Celsius.

Hydrotrope compounds include the compounds listed thereafter:

A list of commercial hydrotropes could be found in McCutcheon's Emulsifiers and Detergents published by the McCutcheon division of Manufacturing Confectioners Company. Compounds of interest also include:

1. Nonionic hydrotrope with the following structure:

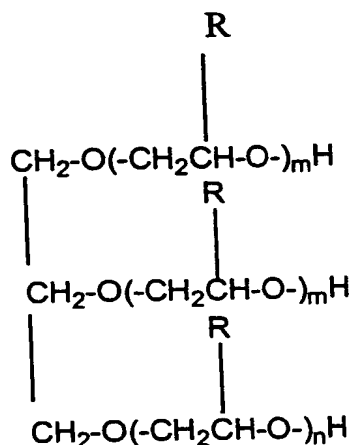


where R is a C8-C10 alkyl chain, x ranges from 1 to 15, y from 3 to 10.

2. Anionic hydrotropes such as alkali metal aryl sulfonates. This includes alkali metal salts of benzoic acid, salicylic acid, benzenesulfonic acid and its many derivatives, naphthoic acid and various hydroaromatic acids. Examples of these are sodium, potassium and ammonium benzene sulfonate salts derived from toluene sulfonic acid, xylene sulfonic acid, cumene sulfonic acid, tetralin sulfonic acid, naphthalene sulfonic acid, methyl- naphthalene sulfonic acid, dimethyl naphthalene sulfonic acid, trimethyl naphthalene sulfonic acid.

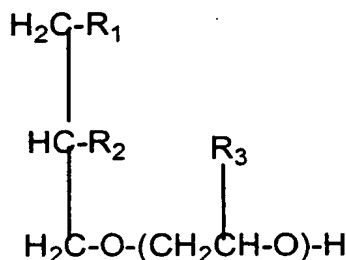
Other examples include salts of dialkyl benzene sulfonic acid such as salts of diisopropyl benzene sulfonic acid, ethyl methyl benzene sulfonic acid, alkyl benzene sulfonic acid with an alkyl chain length with 3 to 10, (pref. 4 to 9), linear or branched alkyl sulfonates with an alkyl chain with 1 to 18 carbons.

3. Solvent hydrotropes such as alkoxyated glycerines and alkoxyated glycerides, esters alkoxyated glycerines, alkoxyated fatty acids, esters of glycerin, polyglycerol esters. Preferred alkoxyated glycerines have the following structure:



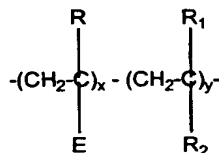
where l, m and n are each a number from 0 to about 20, with l+m+n = from about 2 to about 60, preferably from about 10 to about 45 and R represents H, CH₃ or C₂H₅

Preferred alkoxyated glycerides have the following struture



where R1 and R2 are each C_nCOO or -(CH₂CHR₃-O)_l-H where R₃ = H, CH₃ or C₂H₅ and l is a number from 1 to about 60, n is a number from about 6 to about 24.

4. Polymeric hydrotropes such as those described in EP636687:



where E is a hydrophilic functional group,

R is H or a C1-C10 alkyl group or is a hydrophilic functional group;

R1 is H a lower alkyl group or an aromatic group,

R2 is H or a cyclic alkyl or aromatic group.

The polymer typically has a molecular weight of between about 1000 and 1000000.

5. Hydrotrope of unusual structure such as 5-carboxy-4-hexyl-2-cyclohexene-1-yl octanoic acid (Diacid®)

Use of such compound in the invention would further increase the dissolution rate of the tablet, as a hydrotrope compound facilitates dissolution of surfactants, for example. Such a compound could be formed from a mixture or from a single compound.

Tensile Strength

For the purpose of measuring tensile strength of a layer, the layer may be considered as a tablet itself.

Depending on the composition of the starting material, and the shape of the tablets, the used compacting force may be adjusted to not affect the tensile strength, and the disintegration time in the washing machine. This process may be used to prepare homogenous or layered tablets of any size or shape.

For a cylindrical tablet, the tensile strength corresponds to the diametrical fracture stress (DFS) which is a way to express the strength of a tablet or layer, and is determined by the following equation :

$$\text{Tensile strength} = 2 F / \pi D t$$

Where F is the maximum force (Newton) to cause tensile failure (fracture) measured by a VK 200 tablet hardness tester supplied by Van Kell industries, Inc. D is the diameter of the tablet or layer, and t the thickness of the tablet or layer. For a non round tablet, πD may simply be replaced by the perimeter of the tablet.

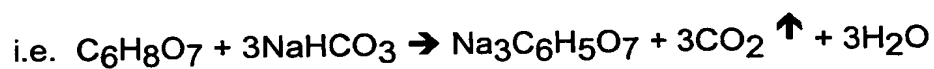
(Method Pharmaceutical Dosage Forms : Tablets Volume 2 Page 213 to 217). A tablet having a diametral fracture stress of less than 20 kPa is considered to be fragile and is likely to result in some broken tablets being delivered to the consumer. A diametral fracture stress of at least 25 kPa is preferred.

This applies similarly to non cylindrical tablets, to define the tensile strength, whereby the cross section normal to the height of the tablet is non round, and whereby the force is applied along a direction perpendicular to the direction of the height of the tablet and normal to the side of the tablet, the side being perpendicular to the non round cross section.

Effervescent

Detergent tablets may further comprise an effervescent.

Effervescency as defined herein means the evolution of bubbles of gas from a liquid, as the result of a chemical reaction between a soluble acid source and an alkali metal carbonate, to produce carbon dioxide gas,



Further examples of acid and carbonate sources and other effervescent systems may be found in : (Pharmaceutical Dosage Forms : Tablets Volume 1 Page 287 to 291).

An effervescent may be added to the tablet mix in addition to the detergent ingredients. The addition of this effervescent to the detergent tablet improves the

disintegration time of the tablet. The amount will preferably be between 5 and 20 % and most preferably between 10 and 20% by weight of the tablet. Preferably the effervescent should be added as an agglomerate of the different particles or as a compact, and not as separated particles.

Due to the gas created by the effervescency in the tablet, the tablet can have a higher D.F.S. and still have the same disintegration time as a tablet without effervescency. When the D.F.S. of the tablet with effervescency is kept the same as a tablet without, the disintegration of the tablet with effervescency will be faster.

Further dissolution aid could be provided by using compounds such as sodium acetate or urea. A list of suitable dissolution aid may also be found in Pharmaceutical Dosage Forms: Tablets, Volume 1, Second edition, Edited by H.A. Lieberman et al, ISBN 0-8247-8044-2.

Detersive surfactants

Surfactant are typically comprised in a detergent composition. The dissolution of surfactants is favoured by the addition of the highly soluble compound.

Nonlimiting examples of surfactants useful herein typically at levels from about 1% to about 55%, by weight, include the conventional C₁₁-C₁₈ alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates ("AS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula $\text{CH}_3(\text{CH}_2)_x(\text{CHOSO}_3\text{-M}^+) \text{CH}_3$ and $\text{CH}_3(\text{CH}_2)_y(\text{CHOSO}_3\text{-M}^+) \text{CH}_2\text{CH}_3$ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C₁₀-18 glycerol ethers, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, and C₁₂-C₁₈ alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C₁₂-C₁₈ alkyl ethoxylates ("AE") including

the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, and the like, can also be included in the overall compositions. The C₁₀-C₁₈ N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts. In a preferred embodiment, the tablet comprises at least 5% per weight of surfactant, more preferably at least 15% per weight, even more preferably at least 25% per weight, and most preferably between 35% and 45% per weight of surfactant.

Non gelling binders

Non gelling binders can be integrated in detergent compositions to further facilitate dissolution.

If non gelling binders are used, suitable non-gelling binders include synthetic organic polymers such as polyethylene glycols, polyvinylpyrrolidones, polyacrylates and water-soluble acrylate copolymers. The handbook of Pharmaceutical Excipients second edition, has the following binders classification: Acacia, Alginic Acid, Carbomer, Carboxymethylcellulose sodium, Dextrin, Ethylcellulose, Gelatin, Guar gum, Hydrogenated vegetable oil type I, Hydroxyethyl cellulose, Hydroxypropyl methylcellulose, Liquid glucose, Magnesium aluminum silicate, Maltodextrin, Methylcellulose, polymethacrylates, povidone, sodium alginate, starch and zein. Most preferable binders also have an active cleaning function in the laundry wash such as cationic polymers, i.e. ethoxylated hexamethylene diamine quaternary compounds, bis-hexamethylene

triamines, or others such as pentaamines, ethoxylated polyethylene amines, maleic acrylic polymers.

Non-gelling binder materials are preferably sprayed on and hence have an appropriate melting point temperature below 90°C, preferably below 70°C and even more preferably below 50°C so as not to damage or degrade the other active ingredients in the matrix. Most preferred are non-aqueous liquid binders (i.e. not in aqueous solution) which may be sprayed in molten form. However, they may also be solid binders incorporated into the matrix by dry addition but which have binding properties within the tablet.

Non-gelling binder materials are preferably used in an amount within the range from 0.1 to 15% of the composition, more preferably below 5% and especially if it is a non laundry active material below 2% by weight of the tablet.

It is preferred that gelling binders, such as nonionic surfactants are avoided in their liquid or molten form. Nonionic surfactants and other gelling binders are not excluded from the compositions, but it is preferred that they be processed into the detergent tablets as components of particulate materials, and not as liquids.

Builders

Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition.

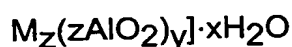
Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the

compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta- Na_2SiO_5 morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $\text{NaMSi}_x\text{O}_{2x+1} \cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

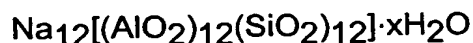
Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites ($x = 0 - 10$) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such

use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Bleach

The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20,

1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

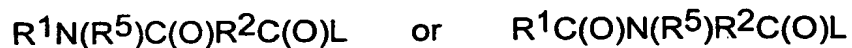
Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the in situ production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

Highly preferred amido-derived bleach activators are those of the formulae:

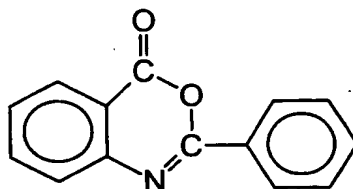


wherein R^1 is an alkyl group containing from about 6 to about 12 carbon atoms, R^2 is an alkylene containing from 1 to about 6 carbon atoms, R^5 is H or alkyl,

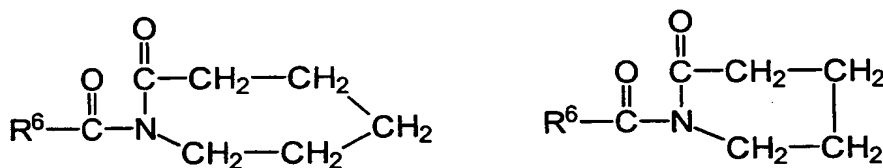
aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein R^6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October

8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_4$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$, $\text{Mn}^{\text{IV}}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{OCH}_3)_3(\text{PF}_6)$, and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.

Enzymes

Enzymes can be included in the formulations herein for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for the prevention of refugee dye transfer, and for fabric restoration. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.01 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease

B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985). Amylases include, for example, α -amylases described in British Patent Specification No. 1,296,839 (Novo), RAPIDASE, International Bio-Synthetics, Inc. and TERMAMYL, Novo Industries.

The cellulase usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgaard et al, issued March 6, 1984, which discloses fungal cellulase produced from *Humicola insolens* and *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk (*Dolabella Auricula* Solander). suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME (Novo) is especially useful.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. The LIPOLASE enzyme derived from *Humicola lanuginosa* and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein. Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish

peroxidase, ligninase, and haloperoxidase such as chloro- and bromoperoxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S.

A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985, both. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868, Hora et al, issued April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patent 3,519,570.

Other components which are commonly used in detergent compositions and which may be incorporated into detergent tablets include chelating agents, soil release agents, soil antiredeposition agents, dispersing agents, suds suppressors, fabric softeners, dye transfer inhibition agents and perfumes.

The compounds disclosed above for a product are advantageously packed in a packaging system.

A packaging system may be formed from a sheet of flexible material. Materials suitable for use as a flexible sheet include mono-layer, co-extruded or laminated films. Such films may comprise various components, such as poly-ethylene, poly-propylene, poly-styrene, poly-ethylene-terephthalate. Preferably, the packaging system is composed of a poly-ethylene and bi-oriented-poly-propylene co-extruded film with an MVTR of less than 5 g/day/m². The MVTR of the packaging system is preferably of less than 10 g/day/m², more preferably of less than 5

g/day/m². The film (2) may have various thicknesses. The thickness should typically be between 10 and 150 μm , preferably between 15 and 120 μm , more preferably between 20 and 100 μm , even more preferably between 25 and 80 μm and most preferably between 30 and 40 μm .

A packaging material preferably comprises a barrier layer typically found with packaging materials having a low oxygen transmission rate, typically of less than 300 cm³/m²/day, preferably of less than 150 cm³/m²/day, more preferably of less than 100 cm³/m²/day, even more preferably of less than 50 cm³/m²/day and most preferably of less than 10 cm³/m²/day. Typical materials having such barrier properties include bi oriented polypropylene, poly ethylene terephthalate, Nylon, poly(ethylene vinyl alcohol) , or laminated materials comprising one of these, as well as SiOx (Silicium oxydes), or metallic foils such as aluminium foils for example. Such packaging material may have a beneficial influence on the stability of the product during storage for example.

Among the packing method used are typically the wrapping methods disclosed in WO92/20593, including flow wrapping or over wrapping. When using such processes, a longitudinal seal is provided, which may be a fin seal or an overlapping seal, after which a first end of the packaging system is closed with a first end seal, followed by closure of the second end with a second end seal. The packaging system may comprise re-closing means as described in WO92/20593. In particular, using a twist, a cold seal or an adhesive is particularly suited. Indeed, a band of cold seal or a band of adhesive may be applied to the surface of the packaging system at a position adjacent to the second end of the packaging system, so that this band may provide both the initial seal and re-closure of the packaging system. In such a case the adhesive or cold seal band may correspond to a region having a cohesive surface, i.e. a surface which will adhere only to another cohesive surface. Such re-closing means may also comprise spacers which will prevent unwanted adhesion. Such spacers are described in WO 95/13225, published on the 18th of May 1995. There may also be a plurality of spacers and a plurality of strips of adhesive material. The main requirement is that the communication between the exterior and the interior of the package should be minimal, even after first opening of the packaging system.

A cold seal may be used, and in particular a grid of cold seal, whereby the cold seal is adapted so as to facilitate opening of the packaging system.

1. A cold seal may be used, and in particular a grid of cold seal, whereby the cold seal is adapted so as to facilitate opening of the packaging system.

EXAMPLES:

Bas tablet composition used in the example

The following composition was prepared by mixing the dry-added materials followed by spraying on of the perfume and binder.

	% Composition
Dry adds	
Anionic surfactant agglomerate A	13.13
Anionic surfactant agglomerate B	21.67
Cationic surfactant agglomerate	5.51
Bleach activator agglomerate	4.53
Zinc Phthalocyanine sulfonate encapsulate	0.025
Suds suppressor	1.88
Layered silicate	10.68
Fluorescer	0.183
Sodium carbonate	13.96
Citric acid	7.17
Sodium percarbonate	14.33
Chelant particle	0.475
HEDP	0.742
Soil release polymer	0.333
Protease prill	0.888
Cellulase prill	0.214
Lipase prill	0.275
Amylase prill	1.042
Soap	1.417
Spray-ons	
Perfume Spray-on	0.458
Binder spray-on	1.083

TOTAL	100%
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Anionic agglomerate A include 40% anionic surfactant, 29% Zeolite and 20% Sodium carbonate.

Anionic agglomerate B include 40% anionic surfactant, 27% Zeolite and 11% Sodium carbonate.

Bleach activator agglomerate comprises 81% TAED, 17% acrylic/maleic copolymer and 2% water.

Zinc Phthalocyanine sulfonate encapsulates are 10% active.

Suds suppressor comprises 11.5% silicone oil and 88.5% starch.

Layered silicate comprises 95% SKS-6, 2.5% Sodium silicate-2.0R and 2.5% water.

Fluorescer contains Brightener 47 (70% active) and Brightener 49 (13% active).

Chelant particle contains ethylene diamine disuccinate and is 58% active.

The binder is polyethoxylated hexamethylene diamine (quaternary salt)

A series of tablets was made according to the following example:

60g of this composition was introduced into a cylindrical tablet die with a diameter 54mm, and compressed using a Lloyd Instruments LR50 testing apparatus to a load of 8.0 kN (rate 10 mm/minute). The resulting tablet was removed from the mould and its diametral fracture stress (s) calculated using the following equation, where F is the force applied to cause fracture (in Newton), D is the tablet diameter (in m) and h is the tablet height (in m). A Vankel VK-200 tablet hardness tester was used to measure the fracture force.

$$s \text{ (in Pa)} = \frac{2F}{\pi Dh}$$

This compression load was found to obtain a tablet of 47kPa diametral fracture stress.

Example

Tablets containing a non-particulate semi-solid phase were prepared according to the following example:

C12-C15 AE7 (alcohol with an average of 7 ethoxylate units) (80g) and PEG4000 (20g) was melted in a water bath at 80°C and mixed thoroughly.

A tablet was placed in a cylindrical mould of equal diameter before pouring 6g of AE7-PEG mixture to the top face of the tablet. After cooling for 16 hours, the tablet was removed from the mould. (PEG stands for Poly Ethylene Glycol).

The non-particulate layer of the tablet was found to be easily transferred onto surfaces by abrasion, as demonstrated by the following protocol. Tablets containing a semi-solid layer were compared with those without such a layer.

A 20cm x 12 cm portion of EMPA Art 300 test fabric (supplied by EMPA testmaterialien) was weighed and then clamped to a work surface at one of the two short sides. A tablet containing a semi-solid layer was weighed and then placed with the semi-solid layer face down on a the test fabric. A string was placed around the tablet and connected to a 908g bell-shaped vinyl covered weight (Aldrich cat no Z15,800-3) hanging off the side of the work surface with a 90cm distance between the tablet and the weight, the weight being 10 cm above its final resting place in such a way as to allow the weight to draw the tablet horizontally across the mesh surface. Another 908g weight was placed on top of the tablet to simulate a consumer pretreatment. The tablet was then drawn 10cm along the fabric as the suspended weight fell a distance of 10cm. The fabric was turned over to release any loose material then weighed to determine the mass difference of the fabric before and after the test. The tablet was then re-weighed and the percentage of material lost by the tablet but transferred adhesively to the fabric calculated.

It was found that material removed from tablets with a semi-solid layer predominantly adhered to the mesh, as illustrated by comparison to similar tablets without such a layer being added.

50 kPa tablets without semi-solid layer			50 kPa tablets with semi-solid layer		
Tablet Weight Loss	Weight adhering to fabric	% Adherence	Tablet Weight Loss	Weight adhering to fabric	% Adherence
0.06g	0.00g	0%	0.17g	0.16g	94.0%

Laundry test results

A comparative laundry test was carried out in a Miele 820 washing machine (Short 40°C cycle, 11.2 grains per gallon hardness) to evaluate the performance benefits of using tablets containing a semi-solid phase to pretreat stains prior to laundering.

Stained swatches were pretreated manually using the semi-solid phase of the tablet prior to laundering with the remaining tablet. Two tablets were used per load and the pretreatment layer of the tablets was applied by abrasion to afford near-complete transfer onto the ten stains (Clay, Lipstick, make-up, eye shadow, shoe-polish, curry, grass/mud, mascara, spaghetti sauce and chocolate ice-cream) used in the test. The remainder of the tablets were dosed in the drum of a front-loading using a simple drawstring net as a dispensing device.

The reference product was identical without a pretreatment step. Significant stain removal benefits were achieved on six (Clay, Lipstick, make-up, eye shadow, shoe-polish, curry) of the ten stains by using the tablet for pretreatment immediately prior to laundering.